

U-Pb sensitive high-resolution ion microprobe ages from the Doushantuo Formation in south China: Constraints on late Neoproterozoic glaciations

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ABSTRACT

Two distinctive volcanic ash beds were found in the terminal Proterozoic Doushantuo Formation in south China. The lower ash bed, ~2.5 m above the cap carbonate at the base of the Doushantuo, yields a U-Pb zircon age of 621 ± 7 Ma, providing the closest upper limit for a correlative of the Marinoan glaciation. The upper ash bed, near the Doushantuo-Dengying boundary, yields a U-Pb zircon age of 555.2 ± 6.1 Ma, providing for the first time a direct age determination for a prominent negative $\delta^{13}\text{C}$ excursion ($\leq -5\%$) above the Marinoan glacial level. This excursion, if interpreted to be of glacial origin, is much younger than the Gaskiers Formation (ca. 580 Ma) in Newfoundland, and perhaps the fifth or sixth such level in the Neoproterozoic. That interpretation, however, is not supported by the proliferation of organisms within strata encompassing the negative $\delta^{13}\text{C}$ excursion in south China and globally, by the lack of a ca. 555 Ma glacial record, and by the absence of stratigraphic evidence for sea-level change. The data call for alternative paleoceanographic models for the origin of Neoproterozoic $\delta^{13}\text{C}$ excursions not clearly related to glaciation.

Keywords: U-Pb, SHRIMP geochronology, Neoproterozoic glaciation, cap carbonates, south China.

INTRODUCTION

Severe glaciations during late Neoproterozoic time (ca. 720–543 Ma) are hypothesized by some to have profoundly influenced early animal evolution (Hoffman et al., 1998; Hoffman and Schrag, 2002; Knoll et al., 2004). Yet the nature of environmental forcing on biological innovation remains uncertain, with considerable debate on the number, magnitude, and synchrony of glaciations (e.g., Evans, 2000; Eyles and Janaszczak, 2004) and their relationship to unusually negative carbon isotopic excursions. On the basis of chemostratigraphic correlation, some authors (e.g., Kaufman et al., 1997) proposed that four or likely five glaciations occurred during the late Neoproterozoic, whereas others (e.g., Kennedy et al., 1998) provided evidence for as few as two of global significance. Recent U-Pb ages from glacial successions in Oman (723 ± 16 – 10 Ma; Brasier et al., 2000), Namibia (635.5 ± 1.2 Ma; Hoffmann et al., 2004), and Newfoundland (ca. 580 Ma; Bowring et al., 2003) seem to support the inference of at least three glaciations, termed Sturtian, Marinoan,

and Gaskiers (or Varanger), respectively. U-Pb ages of 685 ± 7 Ma and 684 ± 4 Ma from a glacial succession of Sturtian age in central Idaho (Edwardsburg Formation; Lund et al., 2003) and ages of 717 ± 4 Ma, 709 ± 5 Ma, and 667 ± 5 Ma in southeastern Idaho (Pocatello Formation; Fanning and Link, 2004), along with a 663 ± 4 Ma date from strata between Sturtian and Marinoan glacial diamictites in south China (Zhou et al., 2004), are consistent with an ice age of long duration, although one that was likely composed of multiple glacial and interglacial intervals and is patchily recorded in the deposits that remain. Newly obtained U-Pb age constraints for an interpreted Marinoan glaciation in Tasmania, Australia (ca. 582–575 Ma; Calver et al., 2004), also challenge the synchrony of generally accepted Marinoan glacial diamictites and, with the Gaskiers Formation of Newfoundland, imply that the Earth was glaciated at least locally during the newly defined Ediacaran Period (Knoll et al., 2004). Reliable age constraints for the glacial units are very desirable.

No more than two main glacial intervals of presumed Sturtian and Marinoan age are pre-

served in most Neoproterozoic successions, with glacial deposits in nearly every case overlain by unusual so-called cap carbonates associated with strongly negative carbon isotope excursions (e.g., Hoffman et al., 1998; Kennedy et al., 1998; Hoffman and Schrag, 2002; Jiang et al., 2003a). That association of glacial and carbonate rocks has led to the view that apparently younger negative $\delta^{13}\text{C}$ excursions may also correspond with glaciation even where direct evidence is lacking (Kaufman et al., 1997). However, until now, none of these $\delta^{13}\text{C}$ excursions has been reliably dated, precluding a direct test of the hypothesis.

In south China, two main glacial intervals—the older Chang'an Formation and the younger Nantuo Formation (Jiang et al., 2003b) of presumed Sturtian and Marinoan age—have long been recognized; the latter is overlain by a thin (<5 m) cap carbonate similar to that of the Marinoan glacial interval of Australia (Kennedy et al., 1998; Jiang et al., 2003a; Zhou et al., 2004). These strata are overlain by as much as 1000 m of predominantly carbonate rocks, extending upward to the base of the Cambrian. With an age of 663 ± 4 Ma from the interglacial Datangpo Formation and uncertainties in correlating its underlying glaciogenic Tiesiao Formation to Chang'an Formation, Zhou et al. (2004) speculated that the Chang'an may record two glaciations older than 663 ± 4 Ma, while the Nantuo represents the third glaciation of Marinoan age. The negative $\delta^{13}\text{C}$ excursion near the Doushantuo-Dengying boundary (e.g., Lambert et al., 1987; Yang et al., 1999; Zhang et al., 2003) has been correlated to the Gaskiers level (e.g., Chen et al., 2004).

Here we report high-resolution ion microprobe (SHRIMP) U-Pb zircon ages for two ash beds in the Doushantuo Formation in the Yangtze Gorge area of south China (Fig. 1). The age data provide a close upper limit for the Marinoan glacial event and its cap carbonates and the first direct constraint on the age

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of the $\delta^{13}\text{C}$ excursion near the Doushantuo-Dengying boundary. Two interpretations are possible for the latter excursion: one is that it corresponds to a fifth or sixth glaciation of late Neoproterozoic age, and the alternative is that it is unrelated to glaciation.

STRATIGRAPHY AND ASH BEDS

In the Yangtze Gorge area, the Doushantuo Formation directly overlies the Nantuo glacial diamictite and consists of as much as 250 m of carbonate and shale (Fig. 1B). It starts at the base with a 3–5-m-thick cap carbonate, overlain by as much as 100 m of interbedded black shale and shaly limestone with abundant pea-sized phosphorite-chert nodules. The middle to upper part of the Doushantuo consists of 100–120 m of shaly limestone, black shale, and thick dolomite with centimeter-scale chert lentils and nodules and laterally discontinuous chert beds. The topmost 15–20-m-thick interval is composed of black shale and thin layers or lenses of dolomite with scattered phosphorite-chert nodules. The Doushantuo is overlain by as much as 800 m of carbonate rocks (mainly dolomite) of the Dengying Formation, which is overlain by Lower Cambrian phosphorite-bearing shale.

Large acanthomorph acritarchs, multicellular algae, and cyanobacteria have been found in the phosphorite-chert nodules from the lower part of the Doushantuo Formation (Fig. 1B; Zhang et al., 1998). According to Yin (1999), such fossils also appear lower in the succession, at the base of the Doushantuo Formation, ~2 m above the cap carbonate. Better preserved and more diversified species are found in chert nodules and layers in the upper part (Zhang et al., 1998), along with abundant macroscopic algae and possibly animal fossils in the topmost shaly layers—commonly referred to as the Miaohe biota (Figs. 1B, 1C; Ding et al., 1996; Xiao et al., 2002). The Ediacara biota, trace fossils, and possible sponge spicules have been reported from the middle to upper part of the Dengying Formation (Fig. 1B; Sun, 1986; Zhao et al., 1988; Steiner et al., 1993), together with small shelly fossils from near the Cambrian-Precambrian boundary (Zhao et al., 1988).

Two strongly negative $\delta^{13}\text{C}$ excursions have been documented from the lowermost and uppermost Doushantuo Formation, with possibly another between (Fig. 1B; Lambert et al., 1987; Yang et al., 1999; Zhang et al., 2003). The lower $\delta^{13}\text{C}$ excursion is closely associated with the cap carbonate that is typical of Marinoan cap carbonates worldwide, but with much higher variability in $\delta^{13}\text{C}$ values (Jiang et al., 2003a; Zhou et al., 2004). The upper $\delta^{13}\text{C}$ excursion, near the Doushantuo-Dengying boundary, is of comparable mag-

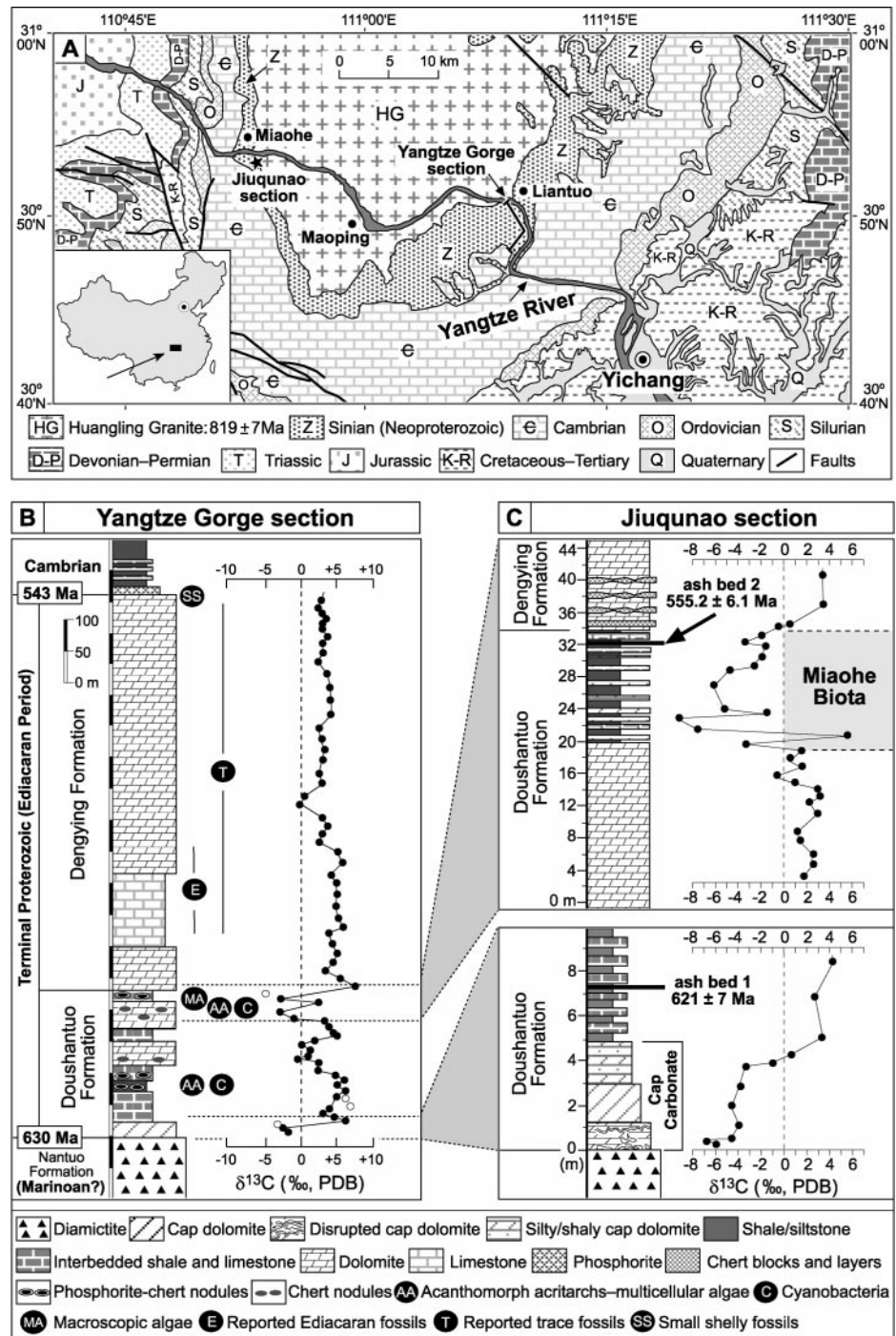


Figure 1. A: Simplified geological map of Yangtze Gorge area, showing locations of typical Yangtze Gorge section and Jiuqudao section of this study (star). B: Lithostratigraphy, biostratigraphy, and chemostratigraphy of Doushantuo and Dengying Formations from Yangtze Gorge section. Fossils are summarized from Ding et al. (1996), Zhang et al. (1998), and Xiao et al. (2002). Isotopic data are adapted from Yang et al. (1999). C: Measured stratigraphic intervals at Jiuqudao with $\delta^{13}\text{C}$ data. Dated ash beds are marked.

nitude and has been correlated with the one in Weng'an, where exceptionally well preserved animal embryo fossils are found (Xiao et al., 1998), and with the Gaskiers glaciation in Newfoundland (Chen et al., 2004). The near zero to slightly negative $\delta^{13}\text{C}$ values in the middle part of the Doushantuo Formation (Fig. 1B) remain an issue, because reported

$\delta^{13}\text{C}$ values at this level are not consistent among different publications.

Ash layers are found in a road-cut section near Jiuqudao, ~30 km west of the Yangtze Gorge type section along the river (Figs. 1A, 1C). The lower ash bed, 4–6 cm thick, is present ~2.5 m above the cap carbonate, slightly postdating the negative to positive $\delta^{13}\text{C}$ tran-

sition (Fig. 1C; Table DR1¹). This ash bed is greenish gray and has been altered to bentonite, mineralogically consisting of illite, mixed-layer illite-smectite, and kaolinite (Zhang et al., 2004). The upper ash bed is found ~1.5 m below the Doushantuo-Dengying boundary, slightly below the negative to positive $\delta^{13}\text{C}$ shift (Fig. 1C; Table DR1 [see footnote 1]) and within the zone in which the Miaohu biota was found (Ding et al., 1996). This ash bed, 3–5 cm thick, is yellowish green and composed of albite, quartz, sanidine, and illite-montmorillonite (Zhang et al., 2004). Both ash beds contain platy and cusped glass shards, indicating contemporaneous volcanic origin.

GEOCHRONOLOGY

The sample from the lower ash bed (04sc20A) contains subeuhedral to euhedral, generally oscillatory zoned zircons from 20 to 110 μm long (Fig. DR1; see footnote 1). Analyses of zircon from this sample yield a weighted-mean $^{206}\text{Pb}/^{238}\text{U}$ age of 621 ± 7 Ma for 13 of the 18 grains analyzed; the mean square of weighted deviates (MSWD) is 1.13 (Fig. 2A; Fig. DR3 and Table DR2 [see footnote 1]). Zircon grains separated from the upper ash bed (04sc21) are euhedral, ranging from 50 to 200 μm , with well-developed oscillatory zonation (Fig. DR2; see footnote 1). Of the 21 zircon grains from this sample, 13 yield a weighted-mean $^{206}\text{Pb}/^{238}\text{U}$ age of 555.2 ± 6.1 Ma, with MSWD of 1.01 (Fig. 2B; Fig. DR4 and Table DR3 [see footnote 1]).

DISCUSSION

An age of 621 ± 7 Ma obtained from the lower ash bed slightly above the cap carbonate provides a direct upper limit for the timing of Nantuo glaciation and the postglacial negative $\delta^{13}\text{C}$ excursion associated with cap carbonates. This age is consistent with Pb-Pb ages of 599 ± 4 Ma (Barfod et al., 2002) and 574 ± 8 Ma (Chen et al., 2004) obtained from the lower and upper phosphorite intervals of the Doushantuo Formation (Weng'an, Guizhou Province), respectively. In combination with the 663 ± 4 Ma age from the Dantangpo Formation underlying the Nantuo Formation (Zhou et al., 2004), glacial deposits of the Nantuo in south China are now constrained to have been deposited between ca. 663 Ma and ca. 621 Ma, a time range that is broadly consistent with age constraints for correlatives of

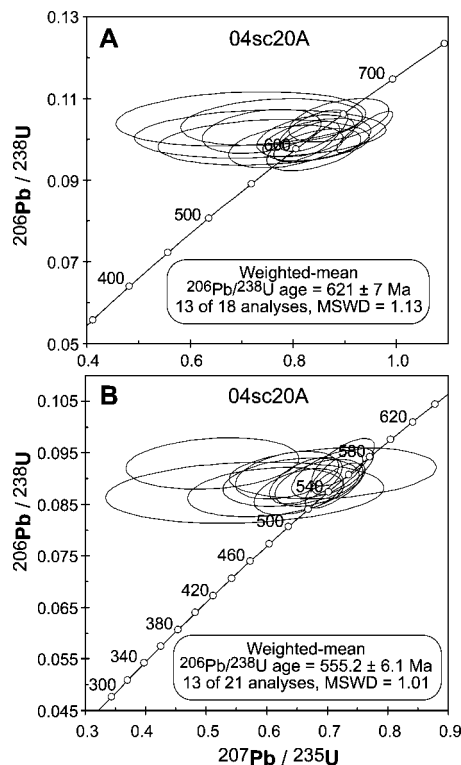


Figure 2. U-Pb concordia plots. A: Lower ash bed (bentonite), sample 04sc20A, ~2.5 m above Doushantuo cap carbonate. B: Upper ash bed, sample 04sc21, near Doushantuo-Dengying boundary. Analyses with 1σ error ellipses are plotted as radiogenic ratios after common Pb correction, using measured ^{204}Pb . Weighted-mean $^{206}\text{Pb}/^{238}\text{U}$ ages at 95% confidence level for main group of zircons show best estimated ages for ash beds. MSWD—mean square of weighted deviates.

the Marinoan glaciation on two other continents. These are a U-Pb age of 635.5 ± 1.2 Ma from the upper part of Ghaub Formation in Namibia (Hoffmann et al., 2004), and an Re-Os isochron age of 607.8 ± 4.7 Ma from postglacial black shales overlying the glaciogenic Mount Vreeland Formation in northwest Canada (Kendall et al., 2004). These data imply that the ca. 585–575 Ma Croles Hill diamictite of Tasmania, Australia (Calver et al., 2004), is significantly younger than the prominent Marinoan event, and most reasonably correlated with the Gaskiers Formation of Newfoundland. Although better precision is needed, the ca. 621 Ma upper limit for the Marinoan cap carbonates suggests that the lower age limit of the newly defined Ediacaran Period (Knoll et al., 2004) should be in the range of ca. 635 Ma to ca. 621 Ma.

The age of 555.2 ± 6.1 Ma from the upper ash bed near the Doushantuo-Dengying boundary provides a significant constraint on the number of Neoproterozoic glaciations and raises questions about the correlation of $\delta^{13}\text{C}$ excursions to the known glacial record. If we interpret the $\delta^{13}\text{C}$ excursion near the Doushantuo-Dengying boundary (Fig. 1) as

glacially related, its ca. 555 Ma age is much younger than the Gaskiers (ca. 580 Ma; Bowring et al., 2003), and even younger than the younger Varanger ice age (ca. 564 Ma) inferred by Saylor et al. (1998) on the basis of $\delta^{13}\text{C}$ excursions in Namibia. If the three pre-Doushantuo glaciations proposed by Zhou et al. (2004) are considered, and the Gaskiers glaciation is counted, the $\delta^{13}\text{C}$ excursion at the Doushantuo-Dengying boundary represents at least the fifth (or the sixth, if the ca. 564 Ma age is accepted) glaciation of the late Neoproterozoic. In this case, the Gaskiers glaciation could be correlated to a zone in the middle Doushantuo Formation, where slightly negative $\delta^{13}\text{C}$ values have been reported to be associated with the dolomite facies (Fig. 1A; Yang et al., 1999; Zhang et al., 2003). Such an interpretation, however, leads to several important but as yet unanswered questions.

First, the ca. 555 Ma $\delta^{13}\text{C}$ excursion in south China was obtained from an interval with perhaps the most abundant and diversified fossil content (Fig. 1). Similarly, proliferating bilaterian body and trace fossils have been reported from strata dated as 555 ± 0.3 Ma in the White Sea region of Russia (Martin et al., 2000), and from the Trepassey Formation (<565 Ma) in Newfoundland, Canada (Narbonne, 2004). If this $\delta^{13}\text{C}$ excursion is considered to have an origin similar to those recognized in postglacial cap carbonates, how could organisms thrive during a severe ice age?

Second, no glacial record of ca. 555 Ma age has been found anywhere in the world. Even if one speculates that glacial deposits were recycled during orogeny, buried beneath sedimentary basins, or not yet discovered, it is unlikely that they were as widespread as those of Sturtian and Marinoan age, implying a much less severe glaciation with perhaps only limited continental ice cover. If the $\leq -5\text{‰}$ shift in $\delta^{13}\text{C}$ near the Doushantuo-Dengying boundary (Fig. 1) is interpreted as glacially related, how could the ocean chemistry change in a similar way and produce $\delta^{13}\text{C}$ excursions of comparable magnitudes when the amount of ice cover on Earth's surface was so different?

Third, widespread glaciation would lead to significant lowering of sea level and result in continental erosion and valley incision. The magnitudes of sea-level change associated with late Pleistocene (Fairbanks, 1989) and Oligocene (eight events; Pekar et al., 2002) glaciations are ~120 m and ~50 m, respectively. Yet a sequence stratigraphic study from the terminal Proterozoic Krol platform in India and the Yangtze platform in south China reveals no obvious erosion at the level of the ca. 555 Ma $\delta^{13}\text{C}$ excursion (Jiang et al., 2002, 2003a), challenging a glacial origin.

¹GSA Data Repository item 2005089, Tables DR1–DR3, carbon and oxygen isotope data and SHRIMP U-Pb zircon data, and Figures DR1–DR4, photomicrographs of dated zircons and plots of age data with accompanying text, is available online at www.geosociety.org/pubs/ft2005.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

CONCLUSION

A U-Pb zircon age of 621 ± 7 Ma from an ash bed (bentonite) ~ 2.5 m above the Doushantuo cap carbonate provides for the first time a firm upper limit for the timing of Marinoan glaciation and its cap carbonates. Although this age is consistent with Pb-Pb dates for Doushantuo phosphorites (599 ± 4 Ma and 574 ± 4 Ma, respectively) and with a U-Pb age for the pre-Marinoan Datangpo Formation (663 ± 4 Ma), the age of 555.2 ± 6.1 Ma for the upper ash bed found in strata associated with a negative $\delta^{13}\text{C}$ excursion near the Doushantuo-Dengying boundary is much younger than the Gaskiers level (ca. 580 Ma). It implies either that the prominent $\delta^{13}\text{C}$ excursion at the Doushantuo-Dengying boundary corresponds to the fifth or sixth Neoproterozoic glaciation, or that the $\delta^{13}\text{C}$ excursion at this horizon has an origin other than global glaciation, because the negative $\delta^{13}\text{C}$ excursion is associated with the proliferation of organisms worldwide, and no evidence for continental glaciation or sea-level change has been recognized at that level.

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